UNIVERSITY OF PENNSYLVANIA

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## I. PREPARATION OF QUINONE

HAROLD EMORY FENIMORE

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA
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## Introduction

During the last half century numerous investigations have been conducted on the electrochemical oxidation of benzene. Some of these researches have resulted in the development of technical methods for producing benzoquinone, and its reduction product, hydroquinone. Others have given valuable information as to the mechanism of the reaction, not only accounting for the production of quinone but also explaining the formation of other products.

Fichter regards phenol as the initial oxidation product of benzene.[1] By electrolyzing a solution of benzene in 2*N* sulfuric acid at a platinum anode in an atmosphere of $CO_2$ at a temperature of 60° a small quantity of phenol has been obtained.[2] Further oxidation of phenol results in the production of o-p′ diphenol and p-p′ diphenol which are oxidized to hydroquinone and pyrocatechol, and quinol respectively.[3] Gattermann and Friedrichs,[4] on electrolyzing a mixture of 20 gms. benzene, 65 cc. alcohol, and 15 cc. 50% sulfuric acid obtained a compound identical in all properties except M. P. with that obtained by Renard.[5] This they identified as quinol. More recently Greenleaf[6] on electrolyzing a solution composed of 120 parts alcohol, 40 parts benzene, 10 parts conc. sulfuric acid and 90 parts water between carbon electrodes at low current density and at a temperature of 5°–10° has obtained an average yield of 25 gms. quinol per kw. hr. That quinol is an intermediate oxidation product between benzene and quinone seems certain, but it may also result from cathodic reduction of quinone where no dia-

[1]Fr. Fichter, Z. Elektrochem., *19*, 781 (1914); see also Trans. Am. Electrochem. Soc., *45*, 109 (1924).

[2]Fichter and Eldor Uhl, Helv. Chim. Acta, *3*, *22* (1920).

[3]Fichter and Robert Stocker, Ber., *47*, 2003 (1914); Fichter and Emile Brunner, Bull. soc. chim., (4), *19*, 281 (1916); M. LeMarchands, Chimie et industrie, *9*, 1180 (1923); see also E. Drechsel, J. prakt. Chem., (2), *29*, *229* (1884); *34*, 135 (1886); *38*, 65 (1888).

[4]Gattermann and Friedrichs, Ber., *27*, 1942 (1894).

[5]Renard, Compt. rend., *91*, 175 (1880).

[6]A. R. Greenleaf, Met. Chem. Eng., *14*, 560–1 (1916).

phragm is employed. Fichter and Ackermann[7] have shown that with a lead peroxide anode in *N* sulfuric acid, and with a varying current density, a 0.2*N* solution of catechol is a more active depolarizer than quinol, or phenol. Only at very low concentrations with a platinum anode in 2*N* sulfuric acid is quinol the more active depolarizer. Hence catechol never accumulates in the presence of quinol, but is further oxidized immediately to fumaric acid (with a diaphragm) or CO, $CO_2$ formic, butyric and succinic acids and formaldehyde in the absence of a diaphragm. On the other hand quinol is oxidized to the more stable benzoquinone[8] which itself is capable of being electrochemically oxidized to CO, $CO_2$ maleic, formic, racemic and tartaric acids.[9]

Kempf, maintaining a suspension of benzene in 10% sulfuric acid by rapid agitation, electrolyzed the mixture between lead electrodes with a current of 1 amp/dm$^2$ at 4 volts to obtain quinone.[10] Fichter and Stocker [11] on electrolyzing benzene "emulsions" in aqueous solutions of sulfuric, phosphoric, perchloric and nitric acids, with and without a diaphragm, obtained quinol and quinone in all instances. On comparing platinum, lead peroxide and graphite anodes in a dilute sulfuric acid suspension of benzene, it was found that the lead electrodes increased the amount of quinone and quinol formed, i.e., the total current yield to a maximum of 21.3%. Lang[12] devised a technical method applicable to the production of quinones involving the use of manganese salts as oxygen carriers. Claudius in a repetition of Kempf's work found that the addition of a little lead peroxide to the anode mixture accelerated the oxidation.[13] In his later critical review of the principal methods used in the manufacture of quinone[14] the electrolytic method of Kempf appeared to be the

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[7]Fichter and Franz Ackermann, Helv. Chim. Acta, *2*, 583 (1919).
[8]Fichter, Trans. Am. Electrochem. Soc., *45*, 109 and 113 (1924); Fichter and Ackermann, *loc. cit.*; E. Dreschel, *loc. cit.*; see also C. F. Boehringer and Son, D. R. P. 117129 (1900); Liebmann, Z. Elektrochem., *2*, 497 (1896).
[9]Th. Kempf, J. prakt. Chem., (2), *83*, 329 (1911).
[10]Th. Kempf, D. R. P. 117251 (1899).
[11]Fichter and Stocker, *loc. cit.*
[12]Walther Lang, D. R. P. 189178 (1902); U. S. P. 808095 (1905).
[13]Chaveau Claudius, Rev. prod. chim., *21*, 219 (1918).
[14]*Ibid.*, 288 (1918).

best, 65–70% of the oxidized benzene being converted to quinone with a current of 3–4 amps/dm² anode at 3–4 volts. Kitchen[15] has devised a technical method for producing quinone by introducing the benzene into an electrolyte preferably 10% sulfuric acid so that it rises through the electrolyte in a finely divided state in close contact with an anodic surface of lead peroxide at which it is partially oxidized. The temperature is maintained below 12° C. and current density is 0.5 amp/dm² anode. The quinone dissolves in the excess benzene, the solution thus formed being subjected to repeated electrolytic action until a solution of high quinone content is obtained. The method further provides for the $SO_2$ reduction of the quinone and recovery of the unchanged benzene. Its chief merit is continuity of process. Inoue and Shikata[16] claim to have obtained 77% material yields of quinone on the basis of the benzene used by electrolyzing an "emulsion" of benzene in 4% sodium sulfate solution with lead plates as electrodes, at a current density of 2–3 amps/dm² at 3–5 volts, and a temperature under 20° C. By adding 1% sodium acetate to the anolyte, and using 5% sulfuric acid as catholyte the yield increased to 81.5%.

Seyewetz and Miodon[17] in reviewing the work of Gattermann and Friedrichs, Kempf (and Gottenbourg), Fichter and Stocker, Inoue and Shikata, report: "In attempting to realize in the laboratory the different conditions indicated by these authors we have been able to obtain only small yields in proportion to the electric energy consumed. The best results have been furnished us by the process of Kempf and Gottenbourg, however they have not exceeded 25% of the electric current and 75% of the benzene consumed." They have reported 65% current yields using an electrolyte consisting of 25% sulfuric acid and 33% acetic acid in which was emulsified by continuous agitation two-thirds of its volume of benzene, electrolyzed between lead electrodes separated by a diaphragm, current density, 4 amps/dm² at 3.2–3.5 volts, temperature, 24° C. 1–1.5% lead sulfate was

[15]Frederick T. Kitchen, U. S. P. 1322580 (1919).
[16]Harnshige Inoue and Masuo Shikata, J. Chem. Ind., (Japan) *24,* 567–80 (1921); see also, Chimie et industrie, *7,* 948 (1922).
[17]A. Seyewetz and G. Miodon, Bull. soc. chim., *33,* 449–58 (1923).

used as a catalyst. The concentration of the quinone was not allowed to exceed 1%, the anolyte being transferred to the cathode compartment where the quinone was reduced to quinol, and extracted.

The preceding excerpts from the literature indicate that the electrochemical oxidation of benzene to quinone is not only slow and incomplete, but is attended with side reactions yielding undesirable products. Fichter says, "Unfortunately there is little prospect of directing the reaction so as to produce an approximately quantitative yield of the significant final products, pyrocatechol and quinone."[18]

The greatest problem attending the electrochemical oxidation of benzene is that of overcoming its very slight solubility, a property which renders it a very poor depolarizer. When initial oxidation does ensue the resultant products, being more soluble, are better depolarizers and hence undergo preferential oxidation. Three expedients have been employed to overcome this difficulty: (*a*) "emulsification" by rapid agitation of electrolyte (*b*) the use of a catalyst or oxygen carrier (*c*) the use of organic solvents. The first method is fairly effective, and advantageous even with solutions, but less efficient than solution. The second alternative has been employed only limitedly with benzene, but more widely with its derivatives.[19] The third method has not been extensively used, and presents certain difficulties. Alcohol has been employed as a solvent but being itself an excellent depolarizer doubtless undergoes preferential oxidation as is indicated by the low yields of quinone and quinol.[20] Acetic acid has been used more recently with better success.[21]

The present work was undertaken with the prime object of determining conditions for increasing yields of quinone obtainable by electrochemical oxidation of benzene. Immediate attention was directed to the selection of a suitable solvent, and the study of the electrochemical oxidation of benzene in this solvent.

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[18]Fichter, Trans. Am. Electrochem. Soc., *loc. cit.*

[19]Boehringer, *loc. cit.;* F. Darmstädter, D. R. P. 109012 (1897); Meister, Lucius and Brüning, D. R. P. 172654 (1903).

[20]Renard, *loc. cit.;* Gattermann and Friedrichs, *loc. cit.;* Greenleaf, *loc. cit.*

[21]Seyewetz and Miodon, *loc. cit.*

Acetone, heretofore not employed as a solvent for benzene though for some of its homologues,[22] was selected because of its miscibility with both dilute sulfuric acid and benzene, and its resistance to oxidation, the products of any such possible action not being objectionable.

### Materials and Apparatus

U. S. P.–C. P. sulfuric acid (sp. gr. 1.83) was used in making up acid electrolyte with distilled water. C. P. Acetone showing an analysis:

| | |
|---|---|
| N. V. M. | 0.002% |
| Aldehyde | 0.000 |
| Water insoluble | 0.000 |
| Substances reducing permanganate | 0.000 |

was employed as a partial solvent for the benzene, which was C. P. Crystallizable Benzol with a maximum impurity of 0.037% thiophene. Purified Petroleum Benzine (B. P. 30°–70° C.) was employed as the solvent for extraction of the quinone from the mixed oxidation products. Other chemicals used were the ordinary C. P. quality to be found in any laboratory.

The oxidation was carried out in a two-compartment cell (Figure I) designed in this laboratory after much experimental work with other types of cells. Effective "emulsification" and cooling were the aims in the designing.

The cathodic compartment *C* consisted of a deep cylindrical glass jar, 12.5 × 30 cms. within which was placed the anodic cell *A*. The cathode *N* was made of lead tubing, 4.7 × 7.9 mm. 6.1 meters in length, coiled to fit snugly against the inner wall of the glass jar. Approximately 1 liter of catholyte sufficed to fill the cell to form an effective liquid seal with the cap of the anodic cell.

The anodic compartment *A* was a cylindrical porous earthenware cup, 7.5 × 20 cms. resting within the cathodic cell on sheet cork to reduce vibration and prevent breakage. 2.3 meters of 4.7 × 7.9 mm. lead tubing coiled to fit the anodic cell served

[22]Fichter and Jacques Meyer, Helv. Chim. Acta, *8*, 74 and 285 (1925); Fichter and Max Rinderspacher, Helv. Chim. Acta, *9*, 1097 (1926); *10*, 40 (1927); Fichter and Kashichi Ono, *ibid.*, 45–52.

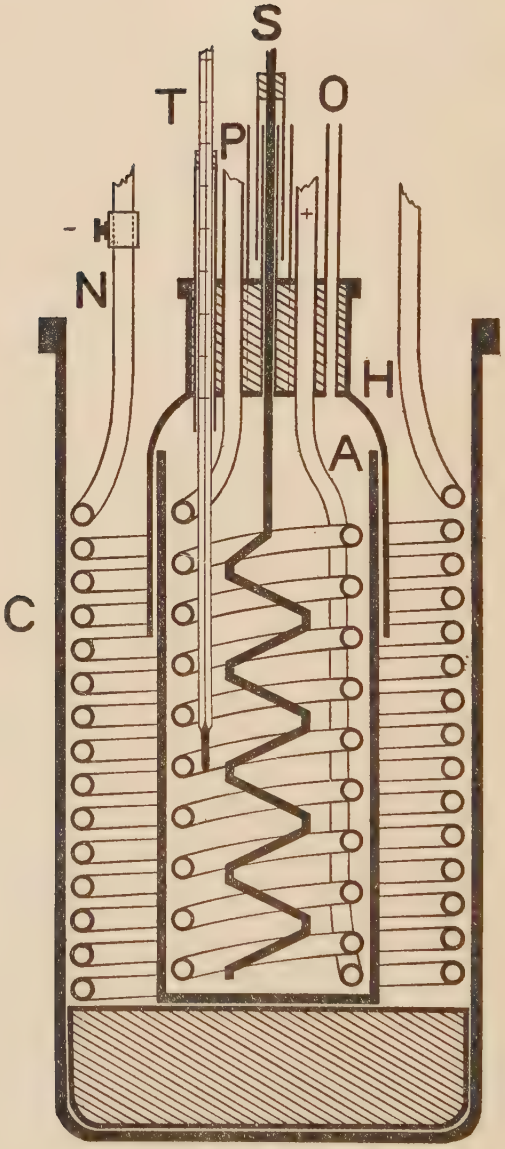


FIGURE 1

as anode *P*. It carried a superficial layer of $PbO_2$ applied electrolytically before each experimental run. The glass stirrer *S* was operated by means of an electric motor at 700–900 r.p.m. through a rigid vertical shaft allowing very little horizontal vibration. Temperature readings were made with a special thermometer *T* having a 14 cm. immersion which enabled readings between 0° and 50° C. without a momentary withdrawal from the anolyte. An outlet tube *O* was provided for the escape of the excess oxygen, and any gaseous products formed in the reaction.

The coil, stirrer shaft and liquid seal cup, and the outlet tube were permanently cemented into a glass cap *H* which fitting over the top of the porous anodic cup with a minimum clearance and projecting down over the outer walls of the cup 7 cms. formed a gas-tight seal with the catholyte on the outside. A tubular opening through the cap permitted the easy removal of the thermometer when the cell was being charged and discharged. With this arrangement it was possible to remove all mechanical parts from the anodic cell as a single unit, facilitating manipulation in charging and discharging. By means of clamps attached to the cap the entire anodic cell was held in perfect alignment with the pulley shaft which operated the stirrer, while the weight of the cathodic cell prevented its movement. The best operating capacity of the anodic cell was found to be approximately 500 cc.

Storage cells supplied current for some of the early work. A generator set consisting of two 6-volt generators connected in series and operated by a motor supplied current for the majority of the reported experiments. Current measurement was made with a Weston D. C. Ammeter (calibrated) across an external shunt. Potential difference was measured with a Weston Volt-Ammeter connected directly across the poles of the cell.

## Procedure

### *Electrochemical Oxidation*

A current of 1 amp. passed through a 10% sulfuric acid electrolyte contained in both compartments of the cell for a period of 10–12 hrs. (usually during the night) sufficed to form an ex-

cellent superficial layer of $PbO_2$ on the anode. Freshly prepared catholyte and anolyte were used to charge the cell. To obtain low temperatures the unit was packed in an ice-salt mixture, and pre-cooled tap water was allowed to flow through the coils until a temperature slightly below that desired for operation was attained. Sufficiently low temperatures could be obtained by connecting the coils in series, i.e., by passing the pre-cooled tap water through the outer cathode coil where it was further cooled by the ice-salt mixture surrounding the outer cell, thence through an insulating rubber tubing connection, through the inner anode coil, and out to the drain. Stirring of the anolyte accelerated this pre-cooling, and prevented local heating during the run, as well as "emulsifying" the benzene in the anolyte. A slight temperature rise always accompanied the passage of the current, but with very little attention it could be maintained within a 2° range. Current of the desired intensity was passed through the electrolyte by regulation of the generator fields. Amperage and voltage readings were taken at regular intervals, usually every 15″ during the first hour, and at 30″ intervals thereafter. No samples were withdrawn from the cell, but the entire anolyte was subjected to the full reaction, the termination of which was determined when a calculated percentage of the theoretical amount of current had passed through the electrolyte.

### *Extraction*

The electrolyzed anolyte was composed of two liquid layers: an upper benzene solution of acetone, dilute sulfuric acid, quinone and other oxidation products, varying in color from a light yellow through a red brown to black; a larger less intensely colored lower layer of an acetone-dilute sulfuric acid solution of the oxidation products also containing some benzene. The sharp odor of quinone was always predominant. When exposed to sunlight for a short period of time the solutions darkened, and on standing, even in the dark, the entire anolyte gradually darkened and a resinous precipitate formed. Meunier and Queroix[23] have investigated the time changes in quinone solutions, and

[23] L. Meunier and M. Queroix, Cuir. tech., *13*, 520–2 (1924).

report that it undergoes a spontaneous oxidation and reduction in solution to form hydroquinol and colored oxidation products of unknown composition, the speed of such change being a function of pH values. Therefore it was found expedient to extract the oxidation products immediately after discharging the anolyte from the cell.

Direct distillation of the electrolyzed anolyte always resulted in a high percentage decomposition of the products.[24] The acetone-benzene-water distillate obtained was colored a light yellow by the quinone carried over with the vapors. Evaporation of the distillate left a residue of yellow needles contaminated by dark oxidation products, the total amount of which never exceeded 2 gms. The dark brown residual liquor in the distilling bulb contained a variable quantity of black resinous material which dried to a brittle, carbonaceous mass easily pulverized. This material, like the resins obtained from solutions on long standing, gave no tests for quinone, but was readily soluble in alcohol and acetone, less soluble in benzene, ether and dilute alkalies.

Steam distillation of the anolyte gave similar results, with even more pronounced decomposition as was evidenced by the increased amount of resins and the less intense color of the distillate obtained.

Reduced pressure distillations were more successful. Under very low pressures the acetone and benzene, with some water, were boiled off at room temperature. Complete condensation, and retention of the distillate in the receiver was found impossible even when the receiver was packed in ice. Small amounts of quinone distilled over and crystallized in pale yellow needles in the receiver as the acetone and benzene boiled off. Doubtless a considerable quantity of the quinone was volatilized simultaneously and lost. After the elimination of the acetone and benzene and with the beginning of the water distillation large quantities of quinone collected in the long cold condenser tube in the form of long golden-yellow needles which were easily washed

[24]See Hugo Stoltzenberg and Margarete Stoltzenberg-Bergius, C. III, 1135 (1921)—Zer. dch. Erhitz. mit siedend Wasser.

out when the distillation was discontinued. While the residual liquor in the distilling bulb contained some resins, the amount was markedly less than when either of the two previous methods was employed.

A fourth method, designated "aëration" method, was tried with variable results. A rapid current of dry air was pulled through the anolyte removing the benzene and a considerable portion of the acetone, with the resultant precipitation of the impure quinone in the dilute sulfuric acid remaining. A series of four ice-cooled traps placed in the line between the suction pump and the aëration flask served as a condensing system for the acetone and benzene. Aërations conducted on the anolyte at temperatures under 30° yielded a product of light brown color, easily filtered by suction, which, when dried in a desiccator and purified, showed a quinone content of 75–85%. Two and one-half to four hours were required to remove the benzene. The longer the aëration was continued, the darker colored the product. Attempts to completely remove the acetone and thus obtain practically a complete precipitation of the quinone resulted in the formation of gummy residues containing a much lower percentage of quinone. For this reason it was found more practical to discontinue the aëration after the benzene was removed, filter out the precipitated products, and then continue the aëration of the filtrate obtaining a smaller second crop of quinone of a lesser degree of purity. The complete removal of the acetone was impossible, hence complete recovery of the dissolved quinone was never accomplished. Additional objections to the method were the inefficiency of the traps in condensing the acetone and benzene, and the volatilization of large amounts of quinone, some of which crystallized in the traps. A reduction in the speed of the air current tended to obviate these difficulties to a slight degree, but so lengthened the time necessary to remove the benzene as to allow pronounced decomposition thus yielding a poor quality product. Aërations conducted at temperatures above 30° C. required less time than those conducted at lower temperatures, gave a higher degree of efficiency to the traps owing to temperature differences, but resulted in a larger percentage

volatilization of quinone, and a very poor quality precipitated product.

A fifth method employed was that of extraction. Both ether and benzene were tried in a modified Schwarz continuous extraction apparatus. Extraction with ether was very unsatisfactory, the process being slow and incomplete, doubtless because of the solubility of the ether itself in the acetone-dilute sulfuric acid-benzene solution. Further, the dark extract yielded resins with very little quinone on the evaporation of the ether. Benzene proved to be a better extraction medium, but also was slow and incomplete, the aqueous-acid solution never being entirely decolorized even after 10 hrs. continuous extraction. The benzene extract was subjected to distillation, the dark impure quinone crystallizing out in an adherent mass on the walls of the flask as the concentration of the solution increased. Removal of this mass for purification purposes was found to be difficult. In some instances a considerable quantity of this material formed on the walls of the extraction flask itself. The acetone-benzene distillate, colored by quinone, was fractionated, the concentrated benzene solution of quinone obtained near the end of the fractionation being used repeatedly as extraction medium for a new batch thus increasing percentage recovery on succeeding runs to a maximum. The impure product yielded 60–75% quinone on purification.

One of the chief difficulties with this method was the necessity of long continued heating of the extract. This always held a considerable quantity of water in solution which materially aided decomposition. Evidence substantiates such a conclusion, for with ether extracts which hold the higher percentage of water, decomposition was more pronounced than with the drier benzene extracts.

To obviate this difficulty cold extraction was resorted to with benzene as the medium. The upper layer of the electrolyzed anolyte was first removed, then the lower aqueous-acid solution subjected to five separate thorough extractions with 200 cc. portions of benzene. While extraction was incomplete, experiment showed that further extracts did not materially increase the final

yield of quinone. These extracts, combined with the benzene layer first removed, were dried over anhydrous sodium sulfate for 6–10 hrs. keeping the solution in the dark. The dried extract subjected to distillation on a water bath, yielded a fairly light colored product which crystallized out in a loosely adhering mass on the walls of the distilling bulb. Decomposition was much less pronounced, purification showing a quinone content of 65–80%.

The acetone-benzene distillate held a small percentage of quinone in solution which was neglected in order to obtain checks on the material yields. A sharp fractionation was found impossible, even with a good column. Dry sodium bisulfite did not react, or at best reacted very slowly with the acetone present. A saturated aqueous solution of the bisulfite, on agitation with the distillate, rapidly eliminated the acetone as the bisulfite compound, leaving the benzene as a clear oily upper layer which was removed, subjected to repeated treatments with fresh bisulfite solution, washed with water, dried over anhydrous calcium chloride and distilled. The recovery was 96–98%, the benzene obtained boiling within a 2° range. This method of separation enabled the calculation of approximate material yields.

### *Purification*

As previously indicated the crude product obtained from the anolyte varied in color from a light yellow to dark brown or black depending on the extraction method used. Attempts to sublime the quinone in a current of air resulted in a rapid darkening of the initial sublimate. Sublimation in an atmosphere of $CO_2$ was little more successful. Two methods were found satisfactory:

(*a*) Volatilization in a rapid current of steam according to Cohen.[25] The product crystallizing in the condenser tube in fine yellow needles was immediately washed out with water, filtered by suction, dried in a desiccator, and preserved in a dark glass bottle. The method yielded an excellent quality of quinone.

[25] Julius B. Cohen, *Practical Organic Chemistry*, Third Edition (1926) p. 226.

There was a slight loss due to decomposition of material in the volatilization flask under the influence of the steam, and a minor loss through solution in the wash water.

(*b*) A new method based on selective solubility. In search for a selective solvent, alcohol, acetone, ether, benzene, toluene, chloroform and carbon tetrachloride were tried with negative results. Using a small amount of commercial pentane (a mixture of hexanes and pentanes) it was found to dissolve the quinone without dissolving the contaminating material, but its low B. P. prevented its extended use. Petroleum benzine which is a mixture of higher homologues of pentane, yielded similar results, the only difference being in the lower degree of solubility of the quinone. With this as extraction medium the method was extended to the treatment of larger quantities of material through the use of a large Soxhlet extractor equipped with a dense alundum thimble. As the extract became concentrated golden-yellow crystals separated out in masses loosely adhering to the flask. Extraction was continued as long as fresh extracts had any color. The extract, cooled to 0°–5° C. was filtered to remove the quinone and returned to the Soxhlet. The crystals, dried rapidly by a few minutes suction, were of a high quality, usually slightly darker than those obtained by the first method. Unlike the residual resins obtained by the first method, the residue was a powdery mass practically free of quinone. The chief requisite was that the crude material should be free from moisture to facilitate extraction with the non-miscible hydrocarbons and to prevent partial decomposition of the quinone in the extraction flask through long heating with water.

### *Identification*

Confirming the physical tests applied to the product, chemical identification was made through the preparation of a quantity of the 2–5 dianilinoquinone[26] as well as through $SO_2$ reduction to hydroquinone.[27] The tetrabromquinone was also prepared and identified.

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[26]Mulliken, *Identification of Pure Organic Compounds,* Vol. I, p. 216.
[27]Identified according to Mulliken, *ibid.,* 108.

### Reduction

To obtain a check on the amount of quinone volatilized with the acetone-benzene distillate from benzene extractions, the distillate was subjected to $SO_2$ reduction, the hydroquinol extracted by repeated washings with water and then extracted from the water with ether. On distilling off the ether a light brown residue of impure hydroquinone was left, which, taken up with water, decolorized with "Darco" and allowed to crystallize from the clear aqueous solution, yielded an excellent quality of material. From the weight of the material obtained an approximate value was calculated for the quinone volatilized with the distillate. This materially increased percentage yields in the few instances where the method was applied. Furthermore, the "washed" acetone-benzene distillate remaining could be subjected to the bisulfite treatment to remove the acetone, recover the benzene, and obtain material yields.

The method was also applied successfully to the aqueous washings obtained when purification method (*a*) was employed. In a few instances where the quinone yield was very low, the purified product, washings and distillate were subjected to reduction and the hydroquinone calculated to quinone.

Direct $SO_2$ reduction of the electrolyzed anolyte without previous treatment yielded a light red-brown solution. After removing the upper layer of benzene, the aqueous-acetone-sulfuric acid solution was extracted with eight 150 cc. portions of ether. A large volume of ether was taken up by the solution, and some acetone was extracted with the ether. Extraction was incomplete, but the extract, subjected to the usual treatment, yielded a very good quality of hydroquinone. No resins formed in the extracted anolyte after standing for more than two weeks.

### Oxidation of Acetone

Fichter and Rinderspacher[28] report that the oxidation of acetone in 2*N* sulfuric acid at a $PbO_2$ anode with a current of 1 amp/dm$^2$ at 20° C. yielded 52% acetic acid with 11.6 amp. hrs.

[28]Fichter and Rinderspacher, Helv. Chim. Acta, *9*, 1097 (1926).

With other material present as a depolarizer it seemed probable that there might be little or no oxidation of the acetone. To test this theory the residual liquid remaining after the extraction of the quinone was subjected to distillation up to the point where large volumes of $SO_2$ were evolved from the decomposition of the sulfuric acid. The clear distillate was carefully neutralized with sodium carbonate and evaporated to dryness on a water bath. 16–18 gms. of salts were thus obtained. Precipitation of the sulfate and carbonate with $BaCl_2$ indicated that these salts constituted 20–25% of the total. Preliminary and confirmatory tests were made on the sodium salts;[29] the acid-para-toluidide corresponding to acetic acid being definitely identified. Additional confirmation was found on heating a portion of the salt with arsenic trioxide to obtain the nauseating odor of cacodyl oxide. Assuming that there were no other salts present except carbonate, sulfate and acetate, the calculated amount of acetic acid produced with over 90 amp. hrs. did not exceed 12 gms. The large recovery of acetone in several different experiments further substantiates the conclusion that the oxidation of the acetone is a negligible quantity. Any acetic acid formed is not objectionable as is indicated by its previously noted use as a solvent for benzene in electrochemical oxidation.

[29]Mulliken, Vol. I, pp. 80–1.

## EXPERIMENTAL DATA

### Table I

| No. | Catholyte | Anolyte | Temperature | Amp/dm² |
|---|---|---|---|---|
| I | 5% $H_2SO_4$ | 50 cc. benzene<br>350 cc. 5% $H_2SO_4$ | 15° C. | 1 |
| II | 10% $H_2SO_4$ | 100 cc. benzene<br>400 cc. 10% $H_2SO_4$ | 11°–19° C. | 3.5–6.5 |
| III | 2% $H_2SO_4$ | 57 cc. benzene<br>500 cc. 4% $Na_2SO_4$ | 13°–19° C. | 2.0–2.5 |
| IV | 5% $H_2SO_4$ | 400 cc. acetone<br>75 cc. benzene<br>25 cc. concentrated $H_2SO_4$ | .... | 1.0–1.3 |
| V | 5% $H_2SO_4$ | 330 cc. acetone<br>45 cc. benzene<br>25 cc. 20% $H_2SO_4$ | .... | 0.5 |
| VI | 5% $H_2SO_4$ | 300 cc. acetone<br>60 cc. benzene<br>25 cc. 50% $H_2SO_4$ | .... | 1.7–2.2 |
| VII | 5% $H_2SO_4$ | 325 cc. acetone<br>100 cc. benzene<br>75 cc. 5% $H_2SO_4$ | 8°–18° C. | 1.0–2.0 |
| VIII | 5% $H_2SO_4$ | 268 cc. acetone<br>82 cc. benzene<br>150 cc. 5% $H_2SO_4$ | 13°–21° C. | 1.0–3.0 |
| IX | 10% $H_2SO_4$ | 300 cc. acetone<br>50 cc. benzene<br>150 cc. 10% $H_2SO_4$ | 12°–21° C. | 1.0–4.0 |
| X | 10% $H_2SO_4$ | 268 cc. acetone<br>82 cc. benzene<br>150 cc. 10% $H_2SO_4$ | 11°–21° C. | 1.0–4.0 |
| XI | 10% $H_2SO_4$ | 200 cc. acetone<br>100 cc. benzene<br>200 cc. 10% $H_2SO_4$ | 14°–19° C. | 2.6–5.9 |
| XII | 20% $H_2SO_4$ | 200 cc. acetone<br>100 cc. benzene<br>200 cc. 10% $H_2SO_4$ | 12°–16° C. | 1.0–2.0 |
| XIII | 20% $H_2SO_4$ | 200 cc. acetone<br>100 cc. benzene<br>200 20% $H_2SO_4$ | 8°–23° C. | 1.0–5.0 |

TABLE I (*continued*)

| No. | Ampere Hours | Voltage | Results |
|---|---|---|---|
| I | 30 | 3–4 | 10–15% current yields of quinone. |
| II | 90–180 | 6.0–6.4 | 12–18% current yields. |
| III | 40–65 | 7.2–9.8 | Less than 20% on basis of current. |
| IV | 10 | 7.0–10 | Traces of quinone; concentrated $H_2SO_4$ reacts with acetone. |
| V | 40 | 25–30 | Traces of quinone; very high resistance of the electrolyte unfavorable. |
| VI | 20 | 8–14 | 12–15% current yield of quinone. |
| VII | 40–60 | 7–35 | 10–42% current yields. |
| VIII | 56 | 20–32 | 20–27% current yields. |
| IX | 54–120 | 7–22 | 20–40% current yields. |
| X | 23–127 | 7–13 | 24–43% current yields. |
| XI | 90–180 | 7–11 | Traces to 45% yields. |
| XII | 36–54 | 3–6 | 40–47% current yields. |
| XIII | 18–180 | 3–11.5 | Traces to 46% current yields. |

TABLE II

ELECTROLYTE VII

| Amp/dm² | Voltage | Ampere Hours | Temperature | Results |
|---|---|---|---|---|
| 0.9–1.7 | 17–32 | 40 | 15–18° | 30–44% current yields. |
| 1.2–2.0 | 7–19 | 40 | 8–12° | 20–26% current yields. |
| | | ELECTROLYTE XIII | | |
| 1.4–4.4 | 5–11.5 | 216 | 18–23° | Only traces of quinone; large quantity of tar. |
| 0.9–1.0 | 3–3.3 | 27 | 12–14° | 40–46% current yields. |
| 0.9–1.0 | 3.2–3.4 | 18 | 8–10° | 35–42% current yields. |
| | | ELECTROLYTE X | | |
| 2.2–2.9 | 6.5–14 | 70 | 17–21° | 24–27% current yields. |
| 2.3–3.2 | 6.5–10 | 70 | 12–15° | 37–43% current yields. |

TABLE III

| Amp/dm² | Voltage | Ampere Hours | Temperature | Results |
|---|---|---|---|---|
| **ELECTROLYTE IX** | | | | |
| 1.0–3.5 | 7.8–22 | 60 | 15–18° | 30–40% current yields. |
| 3.2–3.5 | 8.8–12 | 120 | 14–20° | 20–27% current yields. |
| **ELECTROLYTE X** | | | | |
| 3.3–4.0 | 6.9–7.5 | 23.2 | 12–15° | 35–40% current yields. |
| 2.2–3.2 | 6.5–14 | 70 | 12–21° | 24–43% current yields (see table above). |
| 3.0–3.7 | 6.8–7.9 | 127.6 | 12–15° | 30.3% current yield. |
| **ELECTROLYTE XI** | | | | |
| 3.5–5.0 | 5.5–9.5 | 90 | 14–19° | 25–45% current yields. |
| 2.1–6.0 | 7.5–10 | 153 | 15–16° | Less than 20%. |
| 3.6–5.1 | 7.0–10 | 180 | 15–20° | Traces to 14%. |
| **ELECTROLYTE XIII** | | | | |
| 0.9–1.0 | 3.2–3.4 | 18 | 8–10° | 35–42% current yields. |
| 0.9–1.0 | 3.0–3.3 | 27 | 12–14° | 40–46% current yields. |
| **ELECTROLYTE XII** | | | | |
| 0.9–1.0 | 3.1–3.5 | 36 | 12–14° | 45–47% current yields. |
| 1.8–2.0 | 4.0–5.7 | 54 | 15–16° | Electrolyzed anolyte subjected to $SO_2$ reduction, total yield 25–27% of current. |
| **ELECTROLYTE XIII** | | | | |
| 1.4–4.4 | 5.0–11.5 | 180–216 | 14–23° | At higher temperature only traces of quinone with much tar and unoxidized benzene; 10–15% current yields at lower temperature. |

Calculated anode surface—5.6 dm².
Sulfuric acid concentrations expressed in % volume.
All results are based on the absolute quantity of quinone isolated, or hydroquinone obtained by reduction.

## Discussion

Table I indicates the different types of electrolytes tried with the varying results obtained. Efforts to check the results obtained by Kempf, Inoue and Shikata[30] indicated very low current yields for these methods. With a low percentage of dilute sulfuric acid present, the resistance of the electrolyte is too high to make the electrolysis profitable because of energy consumption, and the development of high temperatures that must be combatted. Concentrated acid reacts with the acetone, especially with temperature increase. Increase in the percentage of dilute acid in the anolyte decreases the solubility of the benzene in the acetone-acid solution, but is offset by the decrease in resistance and lower temperatures during electrolysis.

Table II indicates the effect of temperature. It is to be noted that temperatures above 17°–18° C. are unfavorable to the production of quinone, but result in the production of tars that adhere to the anode, stop further oxidation, or at least reduce such action to a minimum, and increase the resistance very greatly. In at least two instances where the temperature exceeded 20° C. the tars had so completely covered the anode as to render continued oxidation impossible.

Table III shows the effect of prolonged oxidation. While the results indicate that a 15–20% theoretical oxidation yields optimum results, the smaller quantities of quinone in the less oxidized solutions may have been less efficiently extracted by the methods used. Large scale application of the process would involve the removal of the anolyte from the oxidizing zone when 5–10% of the theoretical oxidation had been accomplished, for the quality of the crude quinone rapidly decreases with prolonged oxidation, yielding resinous materials.

Evidence points to a relatively low current density as favorable to current yields. The product obtained is always lighter in color, and material yields attain a maximum of 70–75% at the lower density. Results tabulated indicate that current yields are also higher in most instances.

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[30]Kempf, *loc. cit.;* Inoue and Shikata, *loc. cit.*

Material yields, the best checks for which were obtained on Electrolytes XII and XIII, varied from 60–75%, the highest yields being obtained with Electrolyte XII (see Table III). In those instances where tars were produced in large amounts, material yields were not obtainable.

## Summary

(1) A new electrolyte, involving the use of acetone as a solvent, has been proposed for the electrochemical oxidation of benzene.

(2) A special cell, adaptable to electrochemical oxidations or reductions, has been designed, and the efficiency determined.

(3) Various methods of extraction of the crude quinone from the anolyte have been tried, the results compared, and the cold benzene extraction method selected as the most efficient.

(4) A new method of purification of crude quinone has been devised and successfully applied.

(5) Optimum conditions are determined for the electrochemical oxidation of benzene in the proposed solvent, using the designed cell:

| | |
|---|---|
| Anolyte | 200 cc. acetone<br>100 cc. benzene<br>200 cc. 10–20% sulfuric acid |
| Catholyte | 20% sulfuric acid |
| Current | 0.9–1.0 amp/dm² at 3.0–3.5 v. |
| Temperature | 12°–15° C. |

Anolyte subjected to the action of only 15–20% of the theoretically required current.